DOI: 10.1002/masy.201051036

Studies on the Cure Reaction and Relationship between Network Structure/Thermal Properties of Styrene Copolymers Based on Adypic/Sebacic Acid Modified Unsaturated (Epoxy) Polyesters

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Summary: The studies on the relationship between network structure/thermal properties of styrene copolymers based on adypic/sebacic acid modified unsaturated (epoxy) polyesters cured using different hardeners as well as the course of the cure reaction of polyesters with styrene have been presented. The adypic/sebacic acid modified unsaturated polyesters (UP) prepared from 4-cyclohexene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (MA), adypic acid (AA) or sebacic acid (SA) and ethylene glycol (EG) and their epoxy derivatives: adypic/sebacic acid modified unsaturated epoxy polyesters (UEP) were subjected to the cure process with styrene using diacyl peroxide: benzoyl peroxide (BPO) or the mixture of BPO/suitable acid anhydride: 4-cyclohexene-1,2-dicarboxylic anhydride (THPA) or glutaric anhydride (GA). Thermal properties were evaluated by means of DSC, TG and DMA analyses. It was proved that studied properties were significantly depended on polyester's structure and the type of applied curing system. Generally, higher values of $E'_{20^\circ C}$, $tg\delta_{max}$, E'', ν_e, IDT, T_k for styrene copolymers based on UEP were obtained. It was connected with more cross-linked polymer network structure due to the possible copolymerization reaction of carbon-carbon double bonds of polyester with styrene and additional polyaddition of epoxy to anhydride groups or thermal curing of epoxy groups. The additional connections between polyester's chains led to obtain more stiff and thermal stable polymeric materials. Moreover, the increase of saturated aliphatic acid's chain length in polyester backbone caused the decrease of $E'_{20^\circ C}$, $tg\delta_{max}$, E'', ν_e, IDT, T_k values of styrene copolymers. It suggested that copolymers based on polyesters prepared from acid containing more methylene groups in their structure were characterized by more flexible polymer network due to the "laxity" effect of aliphatic chains.

Keywords: curing of polymers; epoxy; networks; polyesters; resins; structure-property relations; thermal properties; viscoelastic properties

Introduction

Unsaturated polyesters (UP) are usually prepared by polycondensation of combined mixtures, typically of a dihydroxyl compound or mixtures of dihydroxyl compounds (diols) with unsaturated acid/anhydrides under elevated temperature. The commonly used UP are linear polyesters based on maleic anhydride which provides a site for cross-linking. The number and position of double bonds in polyester chain is an important factor responsible for their properties. It makes possible a subsequent curing of polyester with cross-linking agent (e.g. styrene) to polymeric materials using

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suitable initiating system.[1–4] Additionally, modification of UP by the addition of saturated acids/anhydrides during their synthesis allows to reduce the number of double bonds and thus the cross-linking density of obtained cured materials.[5] The most often applied saturated, non-polymerizable acids/anhydrides are phthalic anhydride, aliphatic or cycloolephinic acids or anhydrides.[6] The chemical modification of unsaturated polyesters by introduction of modifying monomers to their synthesis or replace carbon-carbon double bonds in polyester backbone with epoxy, hydroxyl or carboxyl groups leads to prepare new materials with entirely different properties.[7–10] It allows to increase the potential industrial applications of prepared modified polyesters. Recently, the epoxide derivatives of UP containing a large number of epoxy groups offer a considerable interest.[11–19] The chemical modification of UP derivatives of maleic anhydride, 4-cyclohexene-1,2-dicarboxylic anhydride and linear glycols allows to prepare polyesters containing both carbon-carbon double bonds in polyester chain and epoxy groups in cycloaliphatic rings. Such obtained unsaturated epoxy polyesters are able to both polyaddition and copolymerization reactions with vinyl monomer using suitable initiating system.[20–22]

The present paper describes the studies on the relationship between network structure/thermal properties of styrene copolymers based on adypic/sebacic acid modified unsaturated (epoxy) polyesters cured using different hardeners as well as the course of the cure reaction of polyesters with styrene. The adypic/sebacic acid modified unsaturated polyesters (UP) prepared from 4-cyclohexene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (MA), adypic acid (AA) or sebacic acid (SA) and ethylene glycol (EG) and their epoxy derivatives: adypic/sebacic acid modified unsaturated epoxy polyesters (UEP) were subjected to the cure process with styrene using diacyl peroxide: benzoyl peroxide (BPO) or the mixture of BPO/suitable acid anhydride: 4-cyclohexene-1,2-dicarboxylic anhydride (THPA) or glutaric anhydride (GA). The influence of saturated aliphatic acid's chain length as well as the presence of functional groups in polyester backbone on thermal properties has been tested by means of DSC, TG and DMA analyses and discussed.

Experimental Part

Materials

Adypic/sebacic acid modified unsaturated polyesters (UP) were prepared in polycondensation process of 4-cyclohexene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (MA), adypic acid (AA) or sebacic acid (SA) and ethylene glycol (EG). The reaction was carried out at the molar ratio of 1 mol THPA, 0.5 mol MA, 0.5 mol AA or 0.5 mol SA and 2.65 mol EG in the presence of 0.015 wt% of hydroquinone as an inhibitor in the temperature range of 150-180°C.

Adypic/sebacic acid modified unsaturated epoxy polyesters (UEP) were obtained by chemical modification of above described UP with 38-40% peracetic acid. The oxidation process was performed in methylene chloride (1:2) at 40°C for 2h. The raw product was washed with an aqueous solution of sodium carbonate and sodium hydroxide saturated with sodium chloride to neutrality. Then, the organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed by vacuum distillation.[23]

4-cyclohexene-1,2-dicarboxylic anhydride (THPA), maleic anhydride (MA), adypic acid (AA), sebacic acid (SA), 38-40% peracetic acid containing 1wt% of sulphuric acid, methylene chloride and glutaric anhydride (GA) were obtained from Merck-Schuchardt, Hohenbrunn, Germany. Benzoyl peroxide (BPO) and ethylene glycol (EG) were supplied by Fluka, Buchs, Switzerland. Hydroquinone, styrene (ST), sodium carbonate, sodium hydroxide, sodium chloride and magnesium sulphate were delivered by POCh (Gliwice, Poland). All reagents were used as received.

Preparation of Styrene Copolymers Based on Adypic/Sebacic Acid Modified Unsaturated (Epoxy) Polyesters

The styrene solutions of adypic/sebacic acid modified unsaturated (epoxy) polyesters by mixing polyester and styrene in the ratio of 4:1 were prepared. Then, to cure the styrene solutions of adypic/sebacic unsaturated epoxy polyesters (UEP), 1.0wt% of BPO or the mixture of suitable acid anhydride (THPA or GA)/1.0wt% of BPO were added. The stoichiometric ratio of an anhydride r 0.85 were r was defined as anhydride/epoxy groups was applied. Also, to compare the course of the cure reaction and the properties of cured copolymers, the styrene solutions of adypic/sebacic acid modified unsaturated polyesters (UP) prepared in the same concentrations, were cured using 1.0wt% of BPO. The samples used for DSC experiments by mixing styrene with BPO to obtain homogeneous solutions were prepared. Then, the BPO/styrene solutions were added to UEP or UP and tested immediately after mixing. On the contrary, an acid anhydride/BPO compositions were prepared as follows: THPA or GA and UEP were mixed and heated up above the melting point of an anhydride, quenched in cold water and after cooling the solution of BPO and styrene were added, mixed and tested. The samples used for DMA and TGA experiments were additionally conditioned in the temperature range of 100°C - 180°C to obtain the fully cured styrene copolymers. The condition temperatures were appointed from the position of the exothermic peaks at DSC curves. The applied post-cured temperatures allowed to prepare the fully cured styrene copolymers (no additional exothermic peak was appeared in DSC curves).

Techniques

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a NMR Brucker-Avance 300 MSL (Germany) spectrometer at 300 MHz with deuterated chloroform ($CDCl_3$) as the solvent. ^{1}H-NMR chemical shifts in parts per million (ppm) were reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference.

Fourier transform infrared (FTIR) spectra were obtained by using a Perkin-Elmer 1725 X FTIR spectrophotometer in the 400-4000 cm^{-1} wavenumber range using KBr pallets.

The calorimetric measurements were carried out in the Netzsch DSC 204 calorimeter (Germany) operating in a dynamic mode. The non-isothermal scans were performed at a heating rate of 10 K/min from room temperature to a maximum of 500°C under nitrogen atmosphere (30mL/min). As a reference an empty aluminum crucible was used. Thermal characteristic: temperature of the cure initiation (T_{onset}), peak maximum temperature (T_{max}), final cure temperature (T_{end}), the heat generated during the cure reaction (ΔH) as well as thermal degradation temperature (T_d) were evaluated.

Thermogravimetric analysis (TGA) was carried out on a MOM 3427 derivatograph Paulik and Erdey (Hungary) at a heating rate of 10°C/min in air, in the temperature range of 20 - 1000 °C with the sample weight of 100mg. α-Al_2O_3 was used as a reference. The IDT (initial decomposition temperature), the temperature of the maximum rate of weight loss (T_{max}) and final decomposition temperature (T_k) were determined.

DMA measurements were performed using Dynamic Mechanical Analyzer (DMA) Q 800 TA Instruments (USA). Tests were conducted with a double Cantilever device with a support span of 35 mm, calibrated according to the producer's recommendation. Temperature scanning from room temperature until the sample become soft to be tested (180-200°C) with a constant heating rate of 4°C/min at an oscillation frequency of 10Hz was performed. The rectangular profiles of the samples was used (35 × 10 × 4mm). Thermo-mechanical properties of the cross-linked styrene copolymers were estimated from the changes of storage modulus (E'), mechanical loss (E'') as well as from the changes of tanδ at constant frequency depending on temperature. Glass transition temperature (α-relaxation) for obtained copolymers was determined from the dependence of the tanδ on temperature and was identified as the maximum of the tanδ. From the tanδ curves also the width across the curve when it dropped to half of its peak value (FWHM or full-width at half-maximum) and cross-linking density (ν_e) were determined.

Results and Discussion

Characterization of Adypic/Sebacic Acid Modified Unsaturated (Epoxy) Polyesters

Basic properties of adypic/sebacic acid modified unsaturated (epoxy) polyesters in the non-crosslinked state e.g. viscosity (determined by means of a rotating spindle rheometer), density, average molecular weight (determined by osmometric method) and epoxy value (determined by dioxane/HCl titration method) were presented in Tables 1 and 2, respectively.

The structure of adypic/sebacic acid modified unsaturated (epoxy) polyesters was confirmed by FT IR and ^{1}H NMR spectra. Significant differences before and after chemical modification process based on performed analyses were indicated. The disappearance of absorption bands characteristic for double bonds in cyclohexenyl rings at 665, 729 and 776 cm^{-1} (C-H out of plane deformation vibration) and appearance of absorption bands responsible for oxirane ring vibration groups in the range of 789-808 cm^{-1} based on FT IR spectra was observed. Additionally, the absorption bands for carbon-carbon double bonds in polyester chain (C = C stretching vibration) at 1644-1648 cm^{-1} appeared in the spectra for both adypic/sebacic acid modified unsaturated polyesters and epoxy polyesters (Figure 1).

Table 1.
Properties of adypic acid modified unsaturated (epoxy) polyesters.

Properties	Polyester	
	UP	UEP
Viscosity /mPa s	1420	120
Density /g/cm^3	1.12	1.10
Molecular weight /g/mol	720	750
Epoxy value /mol/100g	-	0.24

Table 2.
Properties of sebacic acid modified unsaturated (epoxy) polyesters.

Properties	Polyester	
	UP	UEP
Viscosity /mPa s	1580	200
Density /g/cm^3	1.14	1.12
Molecular weight /g/mol	780	800
Epoxy value /mol/100g	-	0.22

The presence of the characteristic chemical shifts for the protons on the double bonds of cyclohexenyl rings (5.67-5.7 $\times 10^{-6}$) and for the protons on carbon-carbon double bonds of maleic units (6.29-6.35 $\times 10^{-6}$), *cis*-form and (6.90-6.93 $\times 10^{-6}$), *trans*-form for adypic/sebacic acid modified UP were indicated. The disappearance of the peaks for protons assigned to double bonds at cyclohexenyl rings for adypic/sebacic acid modified unsaturated epoxy polyesters was observed. Additionally, the resonance signals attributed to carbon-carbon double bonds for maleic units showed no changes (Figure 2).

Curing Behavior

The course of the cure reaction of styrene solutions of adypic/sebacic acid modified unsaturated (epoxy) polyesters was monitored by means of DSC. To study this process 1.0wt% of diacyl peroxide: benzoyl peroxide (BPO) or the mixture of 1wt% of BPO/suitable acid anhydride: 4-cyclohexene-1,2-dicarboxylic anhydride (THPA) or glutaric anhydride (GA) as initiating system were applied. The one, exothermal, asymmetrical peak for BPO initiated cure reaction of adypic/sebacic acid modified UP with styrene was clearly observed (Figures 3 and 4). The formation of the polymer network for those UP resins may resulted from the competition of various reactions. It was mainly the result of copolymerization of carbon-carbon double bonds of vinyl monomer: styrene with carbon-carbon double bonds in polyester chain. Although, except this, the addition-

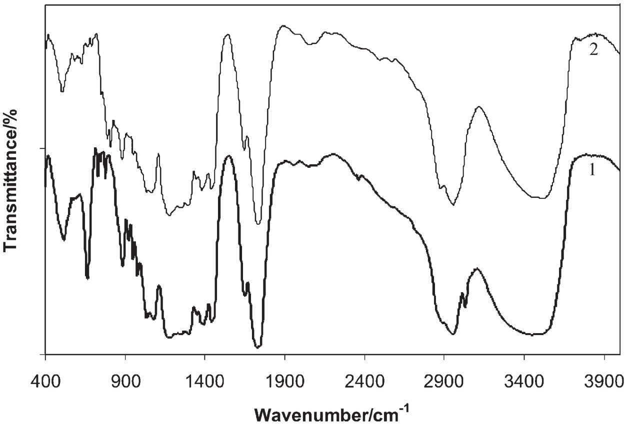

Figure 1.
FT IR spectra of adypic acid modified unsaturated polyester (1) and adypic acid modified unsaturated epoxy polyester (2).

ally homopolymerization of styrene should be also considered.[24,25]

The exothermal effect of BPO cure reaction of adypic/sebacic acid modified UEP with styrene was described by two peaks, one at comparable temperatures observed for cure reaction of adypic/sebacic acid modified UP and the other at

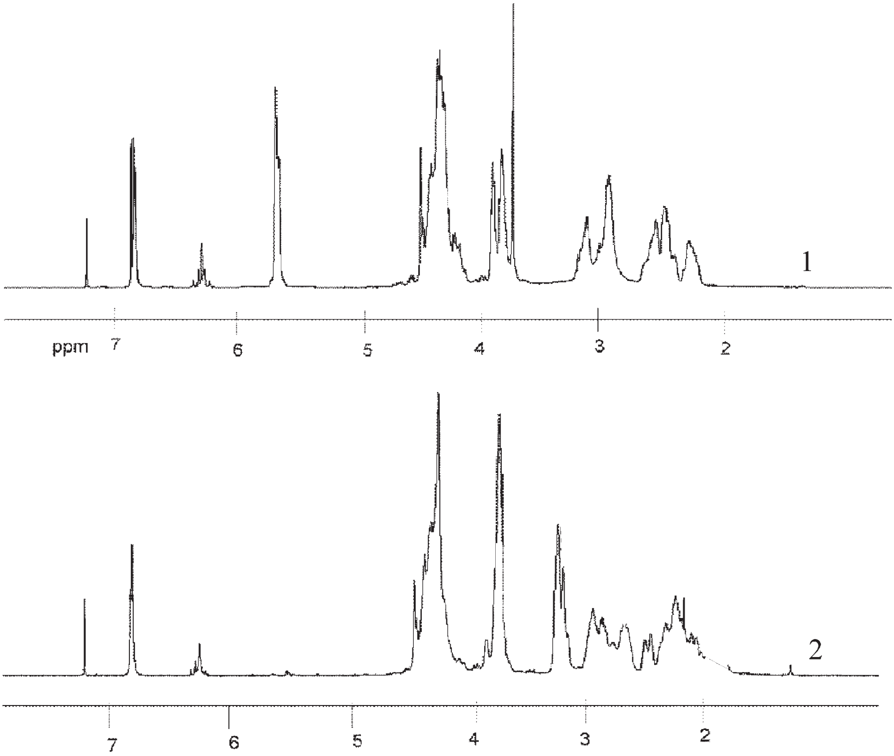

Figure 2.
^{1}H NMR spectra of adypic acid modified unsaturated polyester (1) and adypic acid modified unsaturated epoxy polyester (2).

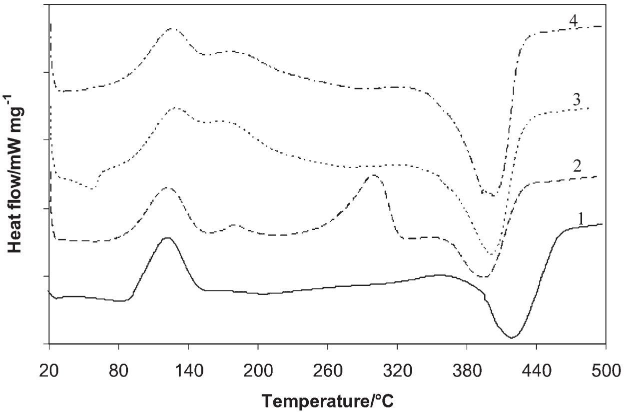

Figure 3.
DSC curves of the cure reaction of adypic acid modified (epoxy) polyesters with styrene: 1 - BPO/UP, 2 - BPO/UEP, 3 - BPO/THPA/UEP, 4 - BPO/GA/UEP.

significantly higher temperatures 298.9 and 312.0°C, respectively (Tables 3, 4). It suggested that in the presence of BPO two cross-linking mechanisms were involved. The first was probably connected with copolymerization process, the second one was due to the thermal curing of epoxy groups with hydroxyl or carboxyl groups in polyester resulting in forming ether or ester linkages at higher temperatures.[24,26,27]

The broad asymmetric, exothermic peak was characteristic for the BPO/acid anhydride cure reaction of adypic/sebacic acid modified UEP with styrene. It indicated on simultaneous copolymerization of carbon-carbon double bonds and polyaddtion reaction of epoxy to anhydride groups. Moreover, the BPO/acid anhydride initiated cure reaction of adypic/sebacic acid modified UEP with styrene started at relatively lower temperatures (T_{onset}) compared to those initiated only with BPO (Tables 3, 4). It may be due to the accelerating effect of an acid anhydride which increased the rate of UEP cure. However, the final cure temperatures (T_{end}) were higher when the cure reaction was initiated with BPO/acid anhydride. The developing skeletal structure of UEP network with additional connections through

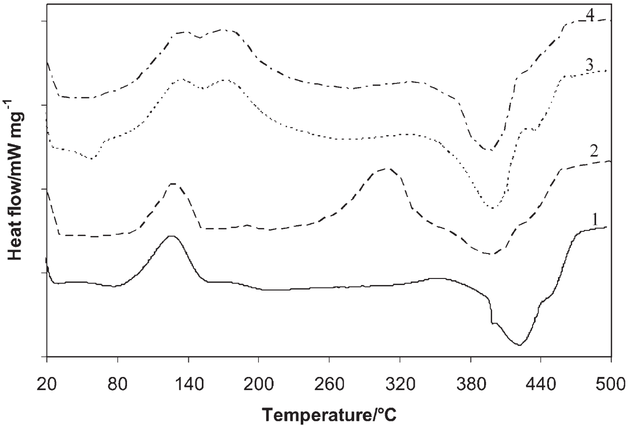

Figure 4.
DSC curves of the cure reaction of sebacic acid modified (epoxy) polyesters with styrene: 1 - BPO/UP, 2 - BPO/UEP, 3 - BPO/THPA/UEP, 4 - BPO/GA/UEP.

Table 3.
DSC data of the cure reaction of adypic acid modified unsaturated (epoxy) polyesters.

Formulation	T_{onset}/°C	T_{max1}/°C	T_{end}/°C	ΔH/kJ mol^{-1}	T_{max2}/°C	T_d/°C
UP/BPO	90.2	121.9	198.7	89.0	-	418.3
UEP/BPO	74.7	121.8/179.9	209.4	88.5	298.9	394.3
UEP/BPO/THPA	61.2	129.4/166.8	268.7	334.5	-	401.0
UEP/BPO/GA	58.6	126.2/174.4	275.3	316.9	-	403.2

Table 4.
DSC data of the cure reaction of sebacic acid modified unsaturated (epoxy) polyesters.

Formulation	T_{onset}/°C	T_{max1}/°C	T_{end}/°C	ΔH/kJ mol^{-1}	T_{max2}/°C	T_d/°C
UP/BPO	89.4	126.7	205.4	84.3	-	421.7
UEP/BPO	78.9	127.4/186.9	207.5	83.2	312.0	390.4
UEP/BPO/THPA	61.5	136.6/171.8	261.3	321.3	-	399.1
UEP/BPO/GA	63.2	132.9/173.3	274.8	302.8	-	398.1

acid anhydride caused to reduce the movement of reacting groups as well as the mobility of polyesters chain. It led to increase the cross-links density of the matrix as the curing process progress and thus decreasing of the rate of cure process.

The heat generated during the BPO initiated cure reaction (ΔH) of adypic/sebacic acid modified UP and UEP was comparable, (Tables 3, 4) indicating the similar amount of unsaturated units in polyester's backbone. Moreover, it was found that the type of used saturated aliphatic acid for polyester's synthesis had a small influence on the course of the cure process. The T_{onset}, T_{max} and T_k values were comparable for both polyesters prepared based on adypic and sebacic acids.

Viscoelastic Properties

The viscoelastic properties of styrene copolymers significantly depended on polyester's structure as well as used curing agent. The BPO cured styrene copolymers based on adypic/sebacic acid modified UP were characterized by significantly lower values of storage modulus ($E'_{20^\circ C}$) compared to BPO cured styrene copolymers based on adypic/sebacic acid modified UEP. It was connected with polyester's structure where UP were only able to copolymerization reaction with styrene due to the presence of carbon-carbon double bonds in polyester chains. The copolymerization with styrene and thermal curing of epoxy groups with initial or reaction formed hydroxyl groups or carboxyl groups in UEP at higher post-cure temperatures have been expected.[27–30] In this way, more stiff network structure for BPO cured UEP was produced.

Similarly, the highest values of storage modulus for BPO/acid anhydride cured styrene copolymers based on adypic/sebacic acid modified UEP were observed. The additionally formed diester linkages during the reaction of acid anhydride groups with epoxy groups caused to produce a more stiff network of copolymers. Additionally, the storage modulus of

Table 5.
DMA data of styrene copolymers based on adypic acid modified unsaturated (epoxy) polyesters.

Formulation	E'_{20}/MPa	$tg\delta_{max}$	$tg\delta_{max}$/°C	E''/°C	$\nu_e * 10^{-3}$ (mol/cm^3)	FWHM/°C
UP/BPO	1650	1.104	40.6	6.7	0.082	–
UEP/BPO	1945	1.047	90.3	68.5	0.533	28
UEP/BPO/THPA	2390	0.646	98.9	73.6	0.952	50
UEP/BPO/GA	2360	1.139	95.9	72.5	0.608	32

Table 6.
DMA data of styrene copolymers based on sebacic acid modified unsaturated (epoxy) polyesters.

Formulation	E'_{20}/MPa	tgδ_{max}	tgδ_{max}/°C	E''/°C	$\nu_e * 10^{-3}$ (mol/cm^3)	FWHM/°C
UP/BPO	16	1.077	-	-	-	-
UEP/BPO	200	1.074	51.8	-	0.207	-
UEP/BPO/THPA	1720	0.879	77.7	55.8	0.423	40
UEP/BPO/GA	1710	1.302	77.6	52.8	0.266	33

styrene copolymers at room temperature (Tables 5, 6) decreased with increasing of aliphatic acid's chain length in polyesters. Generally, the considerably lower values of $E'_{20°C}$ for styrene copolymers based on sebacic acid modified polyesters were obtained. It suggested that copolymers based on polyesters prepared from acid containing more -CH_2- units /methylene groups/ were characterized by more flexible polymeric network structure.

The position of α-relaxation peak (tanδ) as well as loss modulus (E'') clearly depended on polyester's structure and used curing agent, as noted in Tables 5 and 6. The BPO cured styrene copolymers based on adypic acid modified UEP were characterized by significantly higher values of tanδ and E'' compared to BPO cured copolymers based on adypic acid modified UP. Unfortunately, in the studied range of temperatures, no relaxation transition for sebacic acid modified UP was indicated. BPO/acid anhydride cured styrene copolymers exhibited the transition from the glassy state to the rubbery state at a bit higher temperatures compared to others. It was evident due to more cross-linked polymer networks obtained (Figures 5, 6).

Generally, the molecular mobility described as the α-relaxation peak height decreased (lower values of tanδ_{max}) for BPO/THPA styrene copolymers based on adypic/sebacic acid modified UEP. This behavior was connected with larger rigidity of polymer network obtained where the new connections between polyester and styrene and polyester and THPA were formed. However, the increase of tanδ_{max} height for BPO/GA cured styrene copolymers were observed. It was probably due to the presence of aliphatic carbon chain in GA structure and thus causing ''the laxity'' of polymeric network structure obtained.

The cross-linking density (ν_e) for the obtained networks was calculated in order to confirm earlier observations regarding the differences in polymer network's

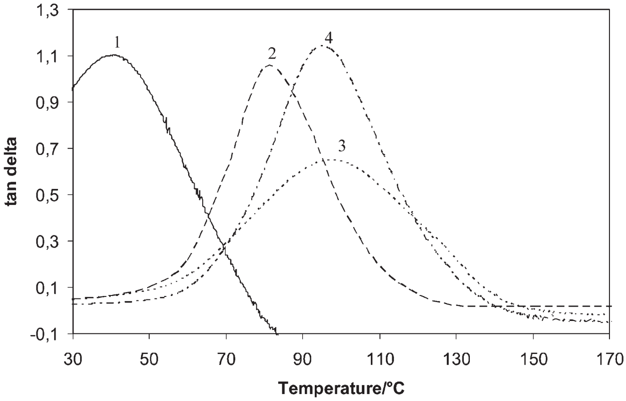

Figure 5.
Tan delta versus temperature curves for styrene copolymers based on adypic acid modified unsaturated (epoxy) polyesters: 1 - BPO/UP, 2 - BPO/UEP, 3 - BPO/THPA/UEP, 4 - BPO/GA/UEP.

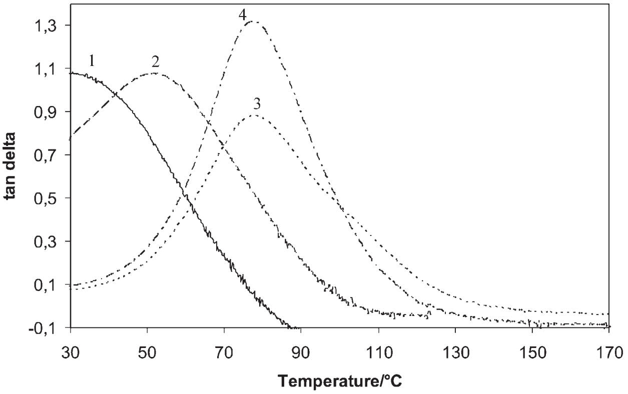

Figure 6.
Tan delta versus temperature curves for styrene copolymers based on sebacic acid modified unsaturated (epoxy) polyesters: 1 - BPO/UP, 2 - BPO/UEP, 3 - BPO/THPA/UEP, 4 - BPO/GA/UEP.

structure. The ν_e values were calculated by applying the equation derived from the theory of rubber elasticity: $E' = 3\ \nu_e\ RT$, where E' is the storage modulus in the rubbery plateau region, R is a gas constant, and T is the absolute temperature.[31–35] Unfortunately, for BPO cured sebacic acid modified UP, the estimation of ν_e value was impossible due to the absence of α-relaxation peak. The higher ν_e values for BPO/THPA cured styrene copolymers based on both adypic/sebacic acid modified UEP compared to BPO cured UEP were observed. Additional diester segments formed in reaction of epoxy groups with THPA groups reduced the molecular motions of polymeric chains. In this way more stiff network structure described by higher cross-linking density and lower molecular weight between cross-links was created.[35] As can be seen, based on Tables 5 and 6, the ν_e values decreased with increase of the aliphatic acid's chain length in polyesters. The higher ν_e values for BPO/THPA cured styrene copolymers prepared from polyester based on adypic acid were observed. Moreover, there was clear relationship between cross-linking density and T_g. When the glass transition temperature decreased the cross-linking density of polymer networks obtained also decreased. The estimation of ν_e values confirmed earlier unusual observations for BPO/GA cured adypic/sebacic acid modified UEP suggesting the preparation of more flexible polymeric networks.

The width of the tanδ curves (FWHM) was connected with the degree of structural heterogeneity of polymer networks. The broader the tanδ peak implied a more heterogeneous polymer network with a wide distribution of relaxation times.[36–39]. The lowest values of FWHM for BPO and BPO/GA cured copolymers based on adypic/sebacic acid modified UEP suggested that more homogeneous network structures were obtained.

Thermal Stability

The thermogravimetric analysis showed the differences in thermal stability of cured styrene copolymers. The TG thermograms indicated that cured styrene copolymers based on adypic/sebacic acid modified UEP were characterized by higher thermal stability than styrene copolymers prepared from UP. The initial decomposition temperatures (IDT) and final decomposition temperatures (T_k) were in the range of 265-300°C and 600-630°, respectively. The IDT and T_k values for all cured styrene copolymers shifted to lower temperatures when sebacic acid was used as modified acid for polyester's preparation. Similarly, BPO/THPA cured styrene copolymers were characterized by higher thermal stability

Table 7.
TG and DTG data of styrene copolymers based on adypic acid modified unsaturated (epoxy) polyesters.

Formulation	IDT/°C	$T_{10\%}$/°C	$T_{20\%}$/°C	$T_{50\%}$/°C	T_k/°C	T_{max1}/°C	T_{max2}/°C
UP/BPO	260	300	330	375	595	375	545
UEP/BPO	275	300	320	370	620	375	540
UEP/BPO/THPA	300	325	345	365	640	370	560
UEP/BPO/GA	290	310	330	370	630	375	560

Table 8.
TG and DTG data of styrene copolymers based on sebacic acid modified unsaturated (epoxy) polyesters.

Formulation	IDT/°C	$T_{10\%}$/°C	$T_{20\%}$/°C	$T_{50\%}$/°C	T_k/°C	T_{max1}/°C	T_{max2}/°C
UP/BPO	240	295	320	370	580	375	535
UEP/BPO	265	300	320	380	600	370	530
UEP/BPO/THPA	290	305	315	365	620	370	530
UEP/BPO/GA	280	300	310	370	620	375	530

compared to others due to the production of more cross-linked polymer network. Moreover, the thermal degradation pattern of all cured styrene copolymers was described by two degradation peaks in DTG curves (Tables 7, 8). The first degradation peak (T_{max1}) observed at 370-375°C was connected with ester bond breakdown in formed network structure.[40,41] However, the second T_{max2} at higher temperatures was mainly the result of total degradation of remaining linkages.

Conclusion

The relationship between network structure/thermal properties of styrene copolymers based on adypic/sebacic acid modified unsaturated (epoxy) polyesters as well as the course of the cure reaction of those polyesters with styrene using different hardeners have been studied. The diacyl peroxide: benzoyl peroxide (BPO) or the mixture of BPO/suitable acid anhydride: 4-cyclohexene-1,2-dicarboxylic anhydride (THPA) or glutaric anhydride (GA) were applied as curing system. Based on performed analyses: DSC, TG and DMA the correlation between network structure/thermal properties has been found. The appointed higher values of $E'_{20^\circ C}$, $tg\delta_{max,}$ E'', ν_e, IDT, T_k for styrene copolymers based on unsaturated epoxy polyesters proved that studied properties were significantly depended on polyester's structure as well as the type of used hardener. The differences in thermal properties were connected with more cross-linked polymer network structure obtained for copolymers of UEP. It was due to the possible various cure reactions: copolymerization of carbon-carbon double bonds of polyester with styrene, polyaddition of epoxy to anhydride groups or thermal curing of epoxy groups. The additional connections through ester or ether linkages between polyester's chains led to obtain more stiff and thermal stable polymeric structure. Moreover, the increase of saturated aliphatic acid's chain length in polyester backbone caused the decrease of $E'_{20^\circ C}$, $tg\delta_{max,}$ E'', ν_e, IDT, T_k values of styrene copolymers. It suggested that copolymers based on polyesters prepared from acid containing more methylene groups in their structure were characterized by more flexible polymer network due to the ''laxity'' effect of aliphatic chains on polymer networks prepared.

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